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IMPROVED CELL NITRIDE NUCLEATION ON INSULATIVE LAYERS AND REDUCED CORNER LEAKAGE OF CONTAINER CAPACITORS

FIELD OF THE INVENTION

10 The present invention relates generally to fabrication of integrated circuit devices and, more particularly, to methods for forming cell nitride layers and capacitors, and capacitor constructions.

BACKGROUND OF THE INVENTION

15 Nitride layers are frequently used in the fabrication of semiconductor wafers, for example, in the fabrication of MOSFET gates, memory cells, and capacitors. The nitride layers are utilized as an insulation layer over silicon surfaces to electrically isolate conductive components of a semiconductor circuit from one another. Nitride films are also used as a diffusion barrier to protect regions of a semiconductor wafer during local oxidation of silicon. In a capacitor, a dielectric nitride layer typically separates the upper and lower conductive plates or electrodes.

20 Various processes are used to produce a nitride layer. One method is by rapid thermal nitridation (RTN), which comprises annealing a silicon layer in an NH_3 or other nitrogen-containing gas that reacts with the silicon to produce silicon nitride. However, the growth of the nitride layer is extremely slow and self-limiting since the NH_3 or other nitrogen-containing gas is not capable of adequately diffusing through the growing silicon nitride layer to react with the underlying silicon.

25 The ultimate thickness of a silicon nitride film produced by nitridation is typically only 3 to 4 nm at high temperatures. Such thickness is usually too low to adequately function as a barrier to prevent further oxidation of the silicon surface during subsequent processing, or as a capacitor dielectric layer between two conductive capacitor plates

30 Surface properties of the wafer surface play an important role in the initial growth of cell nitride films in thin-film processes, which will impact the properties and structure of the thin film that is deposited. Different nucleation and deposition rates occur for the deposition of nitride on different wafer surfaces. This leads to different or degraded electrical characteristics of semiconductor devices having different wafer surfaces that are fabricated using a nitride deposited

layer. In addition, deposition of nitride also includes an incubation time at the start of the deposition where there is no apparent deposition of nitride. The incubation time may extend up to several minutes for some surfaces. Surfaces exhibiting such different rates and incubation times include, for example, borophosphosilicate glass (BPSG), silicon, polysilicon, hemispherical grain (HSG) polysilicon, other doped silicon or polysilicon surfaces, other doped oxides, among others.

An example of a prior art process for forming a DRAM container capacitor is described with reference to **FIGS. 1A-1B**. Referring to **FIG. 1A**, an exemplary semiconductor wafer fragment 10, shown in a preliminary processing step, comprises a substrate 12, an insulative layer 14 of borophosphosilicate glass (BPSG) formed over the substrate, an opening 16 patterned and etched into the BPSG layer 14, and a hemispherical grain (HSG) polysilicon layer 18 formed over the BPSG insulative layer 14 as a bottom electrode or plate of a storage capacitor. As shown in **FIG. 1B**, a nitride dielectric layer 20 is deposited over the HSG silicon layer 18 and the exposed surfaces of the BPSG layer 14. The dielectric layer 20 will typically comprise silicon nitride (Si_3N_4) and/or silicon oxide (SiO_2), with Si_3N_4 being generally preferred due to its higher dielectric constant.

Problems have been encountered in connection with the thickness of the cell nitride layer due to the poor nucleation of cell nitride on BPSG and other insulating materials that form the walls of the container capacitor. Due to the poor nucleation, the cell nitride layer on the insulating (BPSG) layer 14 is substantially thinner than on the overlying electrode layer 18 which can comprise a conductive or semiconductive material such as HSG silicon, which is receptive to nitridation. The non-uniformity of the nitride film deposited on various surfaces is caused by the different surface energies of the different substrates. Consequently, in a subsequent cell nitride wet re-oxidation step, the thin nitride layer on the insulating (BPSG) material cannot prevent the electrode (HSG silicon) layer from oxidation, which causes problems with "punch through" of the nitride layer, which diminishes the function of the capacitor. Also as a result of the poor nitride nucleation on the insulating material (e.g., BPSG), a very thin nitride layer is formed at the top corner area 22 of the container where the electrode (e.g., HSG silicon) intersects with the container wall and the insulating (BPSG) material is exposed. This results in high leakage, i.e., "corner leakage," between the bottom electrode and the top cell plate. Thus, due to the poor nucleation of cell nitride on the insulating (BPSG) material, problems have been encountered with reducing the thickness of cell nitride layers to below 50 angstroms in the manufacture of container capacitors.

A method for forming a uniform nitride layer over different substrate materials is disclosed in U.S. Patent No. 6,235,571 (Doan), which describes forming a uniform dielectric film layer over a

bottom electrode comprising a nitridation receptive material and an insulating material comprising a nitridation resistive material in a storage capacitor fabrication. The method involves depositing a thin layer of non-doped silicon over the bottom electrode and insulating material, and then converting the silicon layer to a silicon nitride compound by thermal nitridation using a nitrogen-containing gas (NH₃). A silicon nitride layer is then deposited to a desired thickness. A disadvantage of this method is that it requires multiple steps to achieve a uniform nitride layer. The deposition of a very thin silicon nitride layer is very difficult to control.

Therefore, it would be desirable to develop a process of forming a cell nitride layer in a capacitor construction that overcomes such problems.

SUMMARY OF THE INVENTION

The present invention encompasses methods of forming a uniform cell nitride dielectric layer in a semiconductor fabrication, methods of incorporating such dielectric layers into capacitor constructions, and capacitors formed from such methods.

In one aspect, the invention provides methods of forming a uniform nitride dielectric film layer onto a substrate comprising a nitride resistive material such as BPSG or other insulating material, and a nitride receptive material such as HSG silicon or other semiconductive material or a conductive material (e.g., conductive metal). In one embodiment of the method, a surface-modifying agent is implanted into the exposed surfaces of the nitride resistive (BPSG) layer to modify the surface of the layer so as to enhance nitride nucleation in the subsequent formation of a nitride cell layer. Examples of suitable surface-modifying agents include ionizable nitrogen and silicon species. The subsequent deposition of nitride results in a substantially uniform thickness of the cell nitride layer over the nitride resistive (BPSG) portion and the nitride receptive (HSG silicon) portion of the substrate.

In another aspect, the invention encompasses methods of forming a capacitor. In one embodiment, the method comprises forming a first capacitor plate comprising a nitride receptive material such as a semiconductive material, for example, HSG polysilicon, in a container comprising an insulation or nitride resistive material such as BPSG; forming a cell nitride dielectric layer over the first capacitor plate; and forming a second capacitor plate over the cell nitride layer. The cell nitride layer is formed after implanting a surface-modifying agent such as an ionizable nitrogen or silicon species, by low angle implantation onto the exposed surfaces of the insulation or nitride resistive (BPSG) layer adjacent the capacitor container and at the top portion and corners of the

container. Preferably, the substrate (e.g., wafer) is rotated during implantation to ensure uniform implantation of the surface-modifying agent into the insulation layer about the circumference of the top portion of the container, including the corners. The modifying agent alters the surface of the insulation layer to enhance nitride nucleation on the insulation layer in the subsequent formation of a nitride cell layer, and achieve a nitride cell layer that has a substantially uniform thickness over the surfaces of the lower electrode and the exposed surfaces of the insulation layer including over the corners of the container.

In another aspect, the invention provides a container capacitor. The capacitor comprises a container formed in a layer of a nitride resistive material such as BPSG or other like insulating material, a lower capacitor electrode comprising a nitride receptive material such as a semiconductive material such as HSG silicon, an upper capacitor electrode, and a nitride dielectric layer formed intermediate the upper and lower electrodes. In an embodiment of a capacitor according to the invention, the exposed surfaces of the insulation layer comprises an implanted species of ionizable nitrogen, silicon or other suitable surface-modifying agent with the overlying cell nitride layer deposited thereon. The capacitor can be incorporated into a semiconductor circuit, including a DRAM cell.

In another aspect, the invention provides an integrated circuit comprising a memory cell array and internal circuitry, and a capacitor fabricated according to the invention that is in electrical contact with an active area within the substrate of the memory cell array.

Semiconductor devices fabricated according to the present invention with a cell nitride insulating layer formed by implanting a surface-modifying agent into the insulation layer (e.g., BPSG) including the top corner portion of an insulative container, and then depositing a cell nitride layer over the lower electrode (e.g., HSG silicon) and exposed surfaces of the insulation layer, have substantially the same electrical performance as conventional devices and improved Cp-leakage performance over a device made with a cell nitride layer alone without the use of a surface-modifying agent as described herein. Also, with the implantation of a surface-modifying agent into the insulation material, the subsequent nucleation and deposition rate of the nitride material upon the different silicon materials (e.g., HSG polysilicon, BPSG) is substantially equivalent regardless of the material. This alleviates the problem of different or degraded electrical characteristics that result from the differences in the nitride thickness deposited on adjacent surfaces, and particularly the corners of a capacitor container that may comprise BPSG. Such differences are especially apparent, for example, between a conductor composed of HSG polysilicon and an insulator composed of

BPSG, where a relatively thin nitride layer deposited at an HSG polysilicon/BPSG edge (e.g., container corner) can result in degraded electrical properties at that edge and for the resulting fabricated device.

The use of the present process of depositing a cell nitride layer also resolves the fatal bubbling and punch-through problems that occur with nitride layers that are deposited directly on insulative substrates in semiconductor devices. In addition, implantation is a well-known technology that is scalable and works well in connection with the trend toward shrinkage of capacitor containers and other semiconductor structures. The invention also allows cell nitride thickness to be scaled down below 50 angstroms and function to prevent "punch through" problems. The thick nitride layer that is deposited by the method of the invention at the top portion of the insulative (BPSG) container at its confluence with the lower (HSG silicon) electrode can avoid problems of top and bottom electrode shorts or high leakage which will increase the reliability of the device.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings, which are for illustrative purposes only. Throughout the following views, the reference numerals will be used in the drawings, and the same reference numerals will be used throughout the several views and in the description to indicate same or like parts.

FIG. 1A is a diagrammatic cross-sectional view of a semiconductor wafer at a preliminary step of a processing sequence according to a prior art method of forming a container capacitor.

FIG. 1B is a view of the wafer fragment of **FIG. 1A** at subsequent and sequential processing steps, showing formation of a cell nitride layer according to a prior art process.

FIG. 2A is a diagrammatic cross-sectional view of a semiconductor wafer at a preliminary step of a processing sequence.

FIGS. 2B-2E are views of the wafer fragment of **FIG. 2A** at subsequent and sequential processing steps, showing fabrication of a capacitor electrode according to an embodiment of a method of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will be described generally with reference to the drawings for the purpose of illustrating the present preferred embodiments only and not for purposes of limiting the same. The figures illustrate processing steps for use in the fabrication of semiconductor devices in accordance

with the present invention. It should be readily apparent that the processing steps are only a portion of the entire fabrication process.

In the current application, the terms “semiconductive wafer fragment” or “wafer fragment” or “wafer” will be understood to mean any construction comprising semiconductor material, including but not limited to bulk semiconductive materials such as a semiconductor wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term “substrate” refers to any supporting structure including, but not limited to, the semiconductive wafer fragments or wafers described above. The term “nitride receptive” material refers to materials that are receptive to nitride nucleation having a relatively shorter nitride nucleation incubation time, such as a conductive metal or other conducting material or silicon HSG silicon or other semiconductive material. The term “nitride resistive” material refers to materials that are unreceptive to nitride nucleation, such as BPSG, oxides, and other materials.

In DRAM (Dynamic Random Access Memory), the capacitors used to store information are generally called “cell capacitors” because they are the unit cells of the memory array. The silicon nitride dielectrics for the cell capacitor is hence generally called “cell nitrides.” In the current application, the term “cell nitride” is used for convenience but it is understood to be exchangeable with the term “silicon nitride” in a broader meaning.

An embodiment of a method of the present invention is described with reference to **FIGS. 2A-2E**, in a method of forming a cell nitride layer in the construction of a container capacitor. While the concepts of the invention are conducive to the fabrication of container capacitors, the concepts described herein can be applied to other semiconductor devices that would likewise benefit from the use of a thin dielectric film that will substantially reduce oxidation punch through. Therefore, the depiction of the invention in reference to the manufacture of a container capacitor is not meant to limit the extent to which one skilled in the art might apply the concepts taught herein.

Referring to **FIG. 2A**, a semiconductor wafer fragment 10' is shown at a preliminary processing step of the method of the invention, and is identical to prior art wafer fragment 10. The wafer fragment 10' in progress can comprise a semiconductor wafer substrate or the wafer along with various process layers formed thereon, including one or more semiconductor layers or other formations, and active or operable portions of semiconductor devices

The wafer fragment 10' is shown as comprising a substrate 12' and an overlying insulation layer 14' (i.e., nitride resistive material). Exemplary insulation materials include silicon dioxide

5 (SiO₂), phosphosilicate glass (PSG), borosilicate glass (BSG), and borophosphosilicate glass (BPSG), in a single layer or multiple layers, with the insulation layer 14'', being BPSG in the illustrated example. A container or opening 16' with sidewalls 24' and a bottom portion 26', has been conventionally etched into the BPSG insulation layer 14'. The lower electrode 18' (i.e., nitride receptive material) of the capacitor comprises a semiconductive material, being HSG polysilicon in the illustrated example. An HSG silicon electrode can be formed, for example, by converting an amorphous silicon layer deposited on the BPSG insulation layer 14' to a hemispherical grain (HSG) silicon layer. The foregoing features can be formed by conventional fabrication methods known and used in the art. As shown, the upper edge of the HSG silicon electrode 18' is slightly lower than the top corner area 22' of the container 16' following a chemical mechanical planarization (CMP) step, thus exposing a portion of the BPSG layer along the container sidewall 24' and corner 22'.

A cell dielectric layer 20' is formed on the BPSG insulation layer 14' and the HSG silicon conductive lower electrode 18'. As noted above, insulating materials such as BPSG, are not readily receptive to nitride nucleation compared to conductive materials such as conductive metals and semiconductive materials such as HSG silicon. However, in forming a container capacitor, it is important to provide a cell dielectric layer that has a substantially uniform thickness over both the HSG silicon surface and the insulative BPSG container surface including at the corners 22' of the container to avoid problems such as punch-through and structure failure.

To achieve this according to an embodiment of the method of the invention, a surface-activating material (agent) 28' is implanted into exposed surfaces of the BPSG insulation layer 14'' adjacent to the container 16' and at the top corner area 22' of the container, as shown in **FIG. 2B**, resulting in the structure shown in **FIG. 2C**. The implantation of the surface-activating agent 28' functions to modify the surface characteristics (i.e., physical and chemical properties) of the BPSG material 14' to enhance nucleation of nitride onto the BPSG layer in a subsequent deposition of cell nitride dielectric material as a layer. A suitable surface-activating agent will reduce the incubation time of the nitride during the film deposition step. Suitable surface-activating agents to improve nitride nucleation on the insulation layer 14' include ionizable species of nitrogen, silicon, or other like species. Exemplary surface-activating agents include a nitrogen-containing gas such as trifluoronitride (NF₃), nitrogen (N₂), ammonia (NH₃), nitrous oxide (N₂O), nitric oxide (NO), and the like; and a silicon source such as silicon tetrafluoride (SiF₄), silane (SiH₄), dichlorosilane (SiH₂Cl₂), trichlorosilane (SiCl₃), silicon tetrachloride (SiCl₄), and the like.

The implantation is generally performed by ion implantation at a low angle of implantation but generally in the range of about 60° to about 85° from vertical, depending on the geometry of the container. The arrows 30' show the low angle implantation at an angle of about 75° from vertical. Due to the container structure, implantation is generally limited to the surface 34' of the BPSG layer adjacent to the container 16' and at the top portion of the container in the proximity of the corners 22'. During the implantation process, it is preferred that the wafer 10' is rotated (arrows 32') to ensure adequate implantation of the surface-activating agent 28' into the BPSG layer 14' along the circumference of the top portion of the container 16' to cover substantially the entire corner area 22'. The arrows 30' show the angle of implantation of the surface-activating agent 28' to limit the implantation to the corner area 22' of the capacitor container and the exposed surface 34' of the BPSG layer 14' so as not to cause damage to the lower electrode 18'. By adjusting the implantation angle and rotating the wafer, a uniform and N-rich (or other species) implantation layer can be generated on the BPSG surface and the container corner section.

A conventional ion implantation process can be used to implant the surface-activating agent 28'. In general, wafers are loaded in one end of an ion implanter (ionization chamber) and the surface-activating agent source (typically in gas form) in the other end of the chamber. The ions implanted are ionized atoms of the surface-activating agent. The chamber is maintained at a low pressure (vacuum) of about 10^{-3} torr. At the source end, the atoms are ionized (given an electrical charge), accelerated to a high speed, and swept across and into the surface 34' of the BPSG layer 14'. The concentration of atoms (i.e., the dose) of the surface-activating agent 28' that are implanted in the BPSG layer is preferably about 10^{12} to about 10^{22} atoms/cm³, preferably about 10^{15} to about 10^{19} atoms/cm³.

Referring now to **FIG. 2D**, a nitride dielectric layer 20' is deposited to a desired thickness over the HSG electrode 18' and exposed surfaces 34' of the BPSG layer 14' including the top corners area 22' of the container. Preferably, the nitride layer 20' is about 100 angstroms or less, preferably about 60 angstroms or less. The deposited nitride layer 20' advantageously has a substantially uniform thickness overlying the BPSG layer 14' and the HSG silicon lower electrode 18'.

A conventional low pressure chemical vapor deposition (LPCVD) process can be used for conformally depositing the cell nitride layer 20', typically by CVD. For example, a film of silicon nitride can be deposited by low pressure chemical vapor deposition (LPCVD) by reacting dichlorosilane (SiH₂Cl₂, DCS) and ammonia (NH₃) over the wafer surface in a hot-wall reactor at

about 600 to about 800°C, a pressure in the range of about 50 mTorr to about 1500 mTorr, and an NH₃:DCS ratio in the range of about 3:1 to about 10:1, preferably about 4:1 to about 6:1. In another example, a conventional LPCVD process can likewise be used for depositing a nitride layer 24' by reacting silicon tetrachloride (SiCl₄) and ammonia (NH₃) at a temperature of about 500°C. to about 800°C., a pressure in the range of about 50 mTorr to about 1500 mTorr, with a NH₃: SiCl₄ ratio in the range of about 10:1 to about 1:2, preferably about 2:1 to about 1:2. The cell nitride layer can also be made by presenting a silicon source gas such as SiH₄, Si₂H₆, and SiH₂Cl₂, among others, and a nitrogen source gas such as N₂ and NH₃ to the deposition chamber using deposition conditions suitable for nitride deposition. Conventional silicon nitride deposition processes other than LPCVD can also be used to deposit the cell nitride layer, including physical deposition, plasma enhanced chemical vapor deposition, and rapid thermal chemical vapor deposition, among others.

The wafer 10' is then subjected to a wet gate reoxidation according to conventional techniques (not shown). The wet oxidation step reduces defects in the cell nitride layer 20' to reduce leakage significantly.

With a consistent, uniform thickness, preferably less than 50 angstroms, the cell nitride dielectric layer 20' has a thickness that is sufficient to prevent oxidation punch-through from the wet oxidation step. Oxidation punch-through refers to the diffusion of atomic oxygen completely through a dielectric film. The oxidation punch-through will cause the HSG silicon electrode to become oxidized, which will diminish the capacitor function. The oxidation punch-through can also adversely affect transistor operation. The electrical field at the edge of the HSG silicon electrode is higher than at other areas. The increased thickness of the cell nitride layer 20' at the corners 22' of the container helps to reduce the corner leakage where the BPSG and HSG silicon materials converge.

Referring now **FIG. 2E**, a conductive material is then deposited over the dielectric layer 20' to form the top capacitor plate electrode 36'. The top electrode 36' comprises a conductive material such as doped polysilicon or a conductive metal. The conductive material can be deposited on the dielectric layer 20' by conventional methods, such as CVD, or physical vapor deposition (e.g., sputtering) for a metal plate, to complete the capacitor structure 40'.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in

any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

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